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HEALTH HAZARD POTENTIAL OF HYPOL (TRADE-MARK) POLYURETHANE PREPOLYMERS

Marlin L. Sweigart, et al

Environmental Health Laboratory
McClellan Air Force Base, California

May 1975

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HEALTH HAZARD POTENTIAL OF HYPOL[®]
POLYURETHANE PREPOLYMERS

By

Marlin L. Sweigart, Captain, USAF
Philip Diamond, Industrial Hygienist

May 1975

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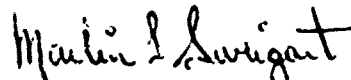
**USAF ENVIRONMENTAL HEALTH LABORATORY
McClellan AFB CA**

**HEALTH HAZARD POTENTIAL OF HYPOL®
POLYURETHANE PREPOLYMERS**

**Prof. Report No 7514-9
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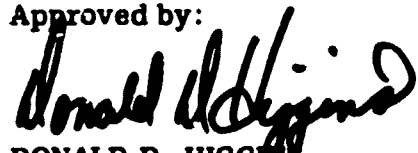
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ABSTRACT

This report presents the results of an evaluation of the potential hazards associated with the use of various formulations of foamable hydrophilic polyisocyanates containing one to two weight percent free toluene diisocyanate (TDI) in Air Force Pacer Foam operations. TDI concentrations and generation rates are presented as well as recommended controls for the use of these prepolymers in foaming operations.

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SECTION I

INTRODUCTION

1. Background: Air Force Packaging and Containerization personnel propose to use two recently developed hydrophilic polyurethane pre-polymers containing one to two weight percent free toluene diisocyanate (TDI) in foam-in-place packaging operations. The prepolymers (HYPOL[®] FHP 2000 and 3000), manufactured by W. R. Grace & Company, Columbia, Maryland, are claimed to have superior fire retardant properties and a wider range of applications than foams presently in industrial use because the cell structure and other properties of the foam can be easily controlled by changing the amount of water and the type of surface - active agent ("Surfactant") used. The Chief, Air Force Packaging Evaluation Agency, Wright-Patterson AFB OH, requested an evaluation of the TDI hazards involved in the use of these prepolymers in Air Force packaging operations.

2. Purpose: This report presents the results of an evaluation of potential TDI exposures of personnel using HYPOL[®] FHP 2000 and FHP 3000 as well as recommendations regarding engineering controls to reduce TDI exposures. The evaluation was conducted at the USAF Environmental Health Laboratory, McClellan AFB CA (USAFEHL-M), from 7 - 21 March 1975.

3. Survey Personnel:

- a. Mr Philip Diamond - Industrial Hygienist, USAFEHL-M.
- b. Capt Marlin L. Sweigart - Bioenvironmental Engineer, USAFEHL-M.
- c. Mr Brick Mesman - Chemist, USAFEHL-M.

4. Personnel Contacted:

- a. Mr Paul Robbins - Chief, Air Force Packaging Evaluation Agency, Wright-Patterson AFB OH.
- b. Capt Bruce H. Dye - Chief, Materials Division, Directorate of Packaging and Containerization, Wright-Patterson AFB OH.
- c. Dr C. L. Kehr - W. R. Grace & Company, Columbia, Maryland.

SECTION II

POLYURETHANE FOAM

1. General: Polyurethane foam is "an expanded cellular plastic product formed by reacting a prepolymer with a polyol blend," (Ref. 1). The resulting cellular structure is open-celled and sponge-like and classified as a flexible packaging material. This product is less expensive and easier to handle than more rigid forms of packaging, and is widely used throughout the Air Force. The Air Force employs various types of polyurethane foam-in-place encapsulation packaging systems and generally refers to them as Pacer Foam Operations.

2. Typical Pacer Foam Operations:

a. The two components in a typical foam-in-place operation consist of a prepolymer designated Component A and a polyol blend designated Component B. They are usually mixed in a 50-50 ratio by volume to produce the final packaging material. The prepolymer component contains the isocyanate portion of the formulation. Component B (the polyol blend) is a mixture of various chemicals, including foam stabilizers (methyl glucoside, sorbitol, sucrose), blowing agents (CO₂, Freon[®] II), flame and fire retardants (phosphate esters, polyesters), and catalysts (amines, polyamines, guidelines, morpholines, organotin compounds, silicones) (Ref. 2). The particular components in any blend depend on the manufacturer and the type of foam desired.

b. The components are mixed manually or mechanically. The manual system consists either of hand mixing or as a batch operation. Mechanical mixing uses various types of dispensing equipment which automatically ration and mix the two components. This equipment usually consists of a spray gun type apparatus which can be either hand held or permanently mounted.

3. HYPOL[®] FHP 2000 and FHP 3000:

a. The HYPOL[®] foam polymer formulations differ in several ways from formulations now in use in Air Force Pacer Foam Operations. These newly developed hydrophilic prepolymers have the ability to form plastic foam with only the addition of water and a surfactant. Component A of these formulations consists of a hydrophilic polyurethane prepolymer containing from one to two percent free TDI, which is the unreacted portion of the original TDI prepolymerized by the addition of a polyol. When water is added to the prepolymerized

urethane the products are a substituted urea and carbon dioxide (CO_2). The CO_2 is the foaming agent in the process. The amount of water added to the HYPOL[®] hydrophilic prepolymer does not have to be carefully adjusted to the stoichiometric equivalent of isocyanate. Rather, a broad range of water to prepolymer ratios can be used. This ability to accept large and relatively uncontrolled amounts of water makes it possible to introduce a wide variety of functional additives in the aqueous stream. These include flame retardants, reinforcing agents, colorants, cleaning agents, etc.

b. The fire retardant properties of HYPOL[®] are claimed to be vastly superior to conventional polyurethane foams. The manufacturer reports a Limiting Oxygen Index (LOI) range for HYPOL[®] foams of 25 to 35 without additives, compared with 15 to 18 for conventional foams. Improved flame retardant characteristics can also be achieved by adding flame retardants to the prepolymer or to the water (Ref. 3). Physical and chemical properties as well as numerous applications of several different HYPOL[®] FHP 3000 and FHP 2000 formulations are presented in Appendix B.

4. Toxicity of TDI:

a. TDI is an irritating material causing both skin and respiratory tract irritation. It is capable of causing irritation by direct contact with the liquid or by exposure to high vapor concentrations. TDI is a sensitizing agent when inhaled. After sensitization workers are subject to asthmatic attacks upon reexposure to very low concentrations of the material in air (Ref. 4). The Threshold Limit Value (TLV) committee of the American Conference of Governmental Industrial Hygienists recommends a "ceiling" TLV for TDI of 0.02 parts per million (ppm), i.e., a concentration that should not be exceeded at any time during exposure (Ref. 5). The National Institute for Occupational Safety & Health (NIOSH) TDI Criteria Document recommends that no worker be exposed to a time-weighted average (TWA) concentration of more than 0.005 ppm for any eight hour work day (Ref. 4).

b. Brief human exposures to concentrations near the TLV have been shown to produce a progressive illness characterized by breathlessness, chest discomfort and reduced pulmonary function. Higher concentrations have caused tracheal and laryngeal irritation and severe coughing spasms, leading to labored respiration and cyanosis (Ref. 6). For an extensive summary of both human and animal exposures to various concentrations of TDI the reader is referred to the NIOSH Criteria Document for Occupational Exposure to Toluene Diisocyanate 1973 (Ref. 4).

SECTION III

AIR SAMPLING PROCEDURES

1. Formulations: As recommended by the Air Force Packaging Evaluation Agency, three different formulations of the HYPOL[®] prepolymer were evaluated. These formulations are shown in Table I.

TABLE I

HYPOL[®] FORMULATIONS

Formulation #1 Regular Foam (HYPOL[®] FHP 3000)

<u>Component A</u>	<u>Component B</u>
100 parts prepolymer FHP 3000	50 parts water
1 part L-520 Silicone Surfactant	

Formulation #2 Regular Foam (HYPOL[®] FHP 3000 With Added TDI For Lower Density)

<u>Component A</u>	<u>Component B</u>
100 parts prepolymer	100 parts water
20 parts TDI	
1 part L-520	

Formulation #3 Regular Angel Foam (TM) (FHP 2000) For Softness Water Wickability

<u>Component A</u>	<u>Component B</u>
20 parts prepolymer	50 parts water
	10 parts pluronic L-64

2. Sampling Procedures:

The formulations were hand mixed in small containers and sealed in Tedlar[®] bags within seconds of the beginning of the rise cycle (see Appendix B, page 4) of the foam. The sealed bags were filled with pure dry air. Impinger samples were taken directly from the bag and analyzed for TDI using the Grim and Linch procedure (Appendix C). Two impinger samples were taken from each bag; a three minute sample was taken starting immediately after the bag was sealed and the dry air added, and a seven minute sample was taken immediately after the three minute sample (see Section IV). The Tedlar[®] bags contained approximately 12 liters of air when filled; thus almost the entire air volume of the bag was sampled during the total 10 minutes of sampling. The weight of the foam produced in each mixing was determined as well as the amount of exposed surface area of the foam. Six air samples were taken using the first formulation, four samples using the second formulation and six samples using the third formulation.

SECTION IV

DISCUSSION AND SAMPLING RESULTS

1. Maximum TDI Generation Phase: One objective of this study was to determine if maximum TDI generation occurred during the rise phase of the reaction. It was expected that most of the TDI generated would be evolved during this phase, i.e., during the first three minutes following mixing of the HYPOL[®] FHP 3000 and FHP 2000 formulations. Bag concentrations were determined for the first three minutes, for the last seven minutes, and for the entire ten minutes of sampling. If maximum TDI generation occurred during the first three minutes, the seven minute and ten minute concentrations were expected to be equal to or slightly greater than the three minute concentrations. As Table II shows, the seven and ten minute samples were actually less than the three minute ones. These low concentrations probably resulted from an interference reaction of the excess water with the free TDI. All three formulations used quantities of water above the exact stoichiometric requirement. The ability to use excess quantities of water in mixing these formulations is considered to be one of the advantages of these prepolymers. The quantities of airborne TDI determined by the Grim and Linch modification of the Marcali Method (Ref. 7) are greatly affected by any moisture in the sampling atmosphere. Marcali attributes this effect to the hydrolysis of TDI to a primary diamine, or other amines which are not detected as free TDI, thus resulting in an unrepresentatively low TDI concentration. During the initial exothermic reaction (the first

TABLE II
TDI CONCENTRATIONS

Sample No	Formula	Volume Air (ℓ)	μg TDI	3 Min Conc. (μg/ℓ)	7 Min Conc. (μg/ℓ)	10 Min Conc. (μg/ℓ)
1	1	3	10.0	3.33		
2	1	7	14.5		2.07	
1 & 2	1	10	24.5			2.45
3	1	3	8.5	2.83		
4	1	7	15.0		2.14	
3 & 4	1	10	23.5			2.35
5	1	3	12.0	4.00		
6	1	7	15.0		2.14	
5 & 6	1	10	27.0			2.70
7	2	3	52.5	17.50		
8	2	7	94.5		13.50	
7 & 8	2	10	147.0			14.70
9	2	3	39.0	13.00		
10	2	7	90.0		12.86	
9 & 10	2	10	129.0			12.90
11	3	3	12.6	4.20		
12	3	7	23.1		3.30	
11 & 12	3	10	35.7			3.57
13	3	3	7.5	2.50		
14	3	7	10.8		1.54	
13 & 14	3	10	18.3			1.83
15	3	3	7.5	2.50		
16	3	7	12.6		1.80	
15 & 16	3	10	20.1			2.01

three minute sample) the excess water was vaporized by the reaction heat. The vaporized water reacted with the free TDI to form a primary diamine which was not diazotized by the sodium nitrate-sodium bromide solution thus indicating a lower TDI concentration than was actually present during the seven minute sampling period. Marcali estimated that TDI concentrations taken in moisturized atmospheres may be as much as 30% lower than the actual concentration (Ref. 7). In his study Dyson, et al (Ref. 8) also showed a maximum reduction of 50 percent for concentrations of 0.4 and 0.034 ppm TDI at relative humidities up to 85%. The reduction depended solely on the water vapor concentration and was fairly rapid. The seven minute concentrations taken in this study actually averaged 29% lower than the three minute concentrations and the overall ten minute concentrations were 20% lower than the three minute ones. This data strongly support Marcali moisture interference theory as well as the original hypothesis that almost all of the TDI was emitted during the rise phase of the reaction.

2. Formulation Variations: Table III shows the airborne TDI concentrations at the end of the initial three minute sampling period. As Table III shows, formulation #2 had produced a significantly higher concentration than the other two mixtures. Formulation # 2 was the only mixture of the three in which free TDI was added to Component A during the mixing. Free TDI is added to increase the amount of CO₂ given off during the reaction. This excess CO₂ provides a greater foaming action which results in a lighter density product.

3. Interferences: The concentrations of TDI found in the sampling bags could have been influenced by several factors which might have altered the final concentrations.

a. As explained in paragraph 1 of this section, the final 10 minute concentrations were probably 30% lower than the actual concentrations due to the interference of excess moisture in the bag.

b. The prepolymer was extremely viscous and difficult to pour and measure. An attempt was made to completely seal the prepolymer container after each test, however, the viscosity gradually increased, indicating crystallization by moisture absorption. Moisture absorption could also have decreased the percent free TDI in the prepolymer due to urea formation and/or volatilization. This could have resulted in TDI concentration lower than would be obtained by using fresh, newly opened prepolymer.

4. TDI Generation Rates: The TDI concentrations shown in Table III are concentrations in the Tedlar[®] bags. In an attempt to relate these

TABLE III
TDI CONCENTRATIONS AND GENERATION RATES

Sample No	Formula	Vol Air (l)	$\mu\text{g TDI}$	ppm	Foam Wt (grms)
1	1	10	33.3	0.467	26.9
2	1	10	28.3	0.397	27.0
3	1	10	40.0	0.562	22.5
4	2	10	175.00	2.475	49.4
5	2	10	130.00	1.825	44.4
6	3	10	42.00	0.590	33.4
7	3	10	25.00	0.351	39.1
8	3	10	25.00	0.351	33.7

Generation Rates:

Formulation 1 = 1.33 $\mu\text{g TDI/gram foam produced}$

Formulation 2 = 3.25 $\mu\text{g TDI/gram foam produced}$

Formulation 3 = 0.87 $\mu\text{g TDI/gram foam produced}$

test concentrations to actual concentrations experienced during Pacer Foam operations, TDI generation rates for the three formulations were calculated. These rates are shown in Table III and give the average number of micrograms of TDI generated per weight of foam produced. As expected Formulation #2 had the highest rate.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

1. Ventilation:

a. These calculated generation rates can be used to design a ventilation system for each particular Pacer Foam operation. They were calculated using the total amount of TDI present in the bags at the end of the initial three minute sampling period. The three minute samples were also subject to TDI loss from moisture interference, therefore ventilation designs should include a sufficient safety factor which allows for at least a 30% higher emission rate.

b. In order to get an idea of the ventilation requirements needed in a Pacer Foam operation utilizing the HYPOL prepolymer, a calculation was made using the physical parameters of the McClellan AFB foam operation. This calculation is presented in Appendix A. With a single flex foam gun pouring 30 lbs/ min of FHP 3000 (Formulation #2) in a 30'x12'x8' room, the McClellan operation would require a minimum 910 air changes/hr just to keep the concentration of TDI at the eight hour NIOSH recommended TWA. Accounting for imperfect mixing, air distribution and safety factors a minimum of 1800 air changes/hr would be required.

c. Because of the recognized high toxicity of TDI and the emission rates calculated, local exhaust ventilation must be provided for any Pacer Foam operation using the HYPOL FHP 3000 or FHP 2000 prepolymer. A local exhaust system would contain the TDI vapors generated during such work and prevent their migration to other work areas. A local exhaust ventilation system similar to a paint spray booth should be provided for the foaming operation.

d. Curing and demold areas should also have local exhaust ventilation; however, the exact design would have to be based on the specific process. If the foam is enclosed in plastic and the boxes closed during the curing process less ventilation would be necessary. On the other hand, if the boxes are left open during the curing process,

a ventilation system similar to the foam area system should be provided.

2. Free TDI Restriction: If the HYPOL[®] prepolymers are utilized in foaming, formulations which include the addition of free TDI to decrease foam density should not be used. These formulations produce a significantly greater amount of TDI vapors than formulations which do not utilize free TDI addition. Lower density foams can be achieved using an auxiliary blowing agent such as Freon[®] 11 in the prepolymer.

3. TDI Reduction In Prepolymer: An attempt should be made by the manufacturer to decrease the amount of free TDI in the prepolymer. The one to two percent free TDI contained in these prepolymers is excessive. In fact the military specifications for these materials states that no free TDI should be present (Ref. 9). Any reduction in the amount of free TDI in the prepolymer would directly reduce the vapor quantities emitted. The manufacturer indicated that a reduction in the amount of free TDI was not economically possible (Ref. 10).

4. Preventive Measures: Safety and health precautions required when handling and foaming of TDI prepolymers can be found in USAF Technical Order (TO) 00-84-37 "Foam-In-Place Packaging" (Ref. 11). These procedures should be followed in detail.

5. If the NIOSH TDI Criteria Document recommended standard is adopted into law an even more extensive and expensive worker protection program will be required where TDI exposure is involved. The recommended standard is shown in Appendix D.

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APPENDIX A

SAMPLE CALCULATIONS

SAMPLE CALCULATION

McClellan Flex Foam Gun capable of producing 30#/min foam

30#/min = 817,200 grams/hr = 5,537,600 gms/8 hr day

Recommended NIOSH TWA = 0.005 ppm for 8 hr day

TLV for TDI = 0.02 ppm for 20 min period

1 ppm of TDI @ STP = 0.00712 mg/l

Then:

$$\frac{0.00712 \text{ mg/l}}{1 \text{ ppm}} \times 0.005 \text{ ppm} = 3.56 \times 10^{-5} \text{ mg/l} = 3.56 \times 10^{-2} \mu\text{g TDI/l}$$

Using the generation rate for the worst case; Formulation #2

Generation Rate = 3.25 $\mu\text{g TDI/gram foam}$

$$3.25 \frac{\mu\text{g TDI}}{\text{gram foam}} \times 6.5 \times 10^6 \text{ grams} = 2.1 \times 10^7 \mu\text{g TDI/day}$$

Volume air needed to keep concentration TDI at TLV would equal

$$\frac{2.1 \times 10^7 \mu\text{g TDI/day}}{3.56 \times 10^{-2} \mu\text{g TDI/l}} = 5.9 \times 10^8 \text{ l air/day}$$

$$\text{Changing to ft}^3 = \frac{5.9 \times 10^8 \text{ l}}{28.3 \text{ l/ft}^3} = 2.1 \times 10^7 \text{ ft}^3 \text{ of air/day}$$

The McClellan Flex Foam Gun is housed in a semi-enclosed area which measures 30'x12'x8'; or a 2880 ft³ area.

To keep the concentration of TDI just below the TLV, the room would require more than;

$$\frac{2.1 \times 10^7 \text{ ft}^3/\text{day}}{2.88 \times 10^3 \text{ ft}^3} = 7300 \text{ air changes/day}$$

$$2.88 \times 10^3 \text{ ft}^3 = 910 \text{ air changes/hr if perfect mixing occurs}$$

However, under most conditions perfect mixing does not occur and;

K of 1.5 for flow through

$$910 \times 1.5 = 1360$$

30% safety factor = 1800 air changes/hr

APPENDIX B
HYPOL[®] FOAM POLYMER CHARACTERISTICS

HYPOL Foam Polymer — What It Is and What It Does

A newly developed hydrophilic polyurethane prepolymer, having the unique ability to form plastic foam with only the addition of water, makes possible a whole new class of foam products.

The new polymer, trade named HYPOL, was developed at W.R. Grace & Co.'s Central Research Division Laboratories in Columbia, Maryland and recently turned over to the company's Dewey and Almy Chemical Division, Cambridge, Massachusetts for commercial introduction.

In contrast to conventional (*hydrophobic*) foam preparation, where 3 to 5 parts of water are used per 100 parts of polymer, the amount of water used with HYPOL hydrophilic foam polymer does not have to be carefully adjusted to the approximate stoichiometric equivalent of isocyanate content. Instead, a broad range of water to prepolymer ratios may be used — from 2,000 to 20,000 percent of the theoretical amount required. In practice, 35 to 200 parts of water are used per 100 parts of prepolymer, depending on the foam characteristics desired. This ability to accept large and relatively uncontrolled amounts of water makes it possible to introduce a wide variety of functional additives in the aqueous stream. These include flame retardants, reinforcing agents, colorants, cleaning agents, etc.

In addition to the non-critical water requirements of HYPOL prepolymer, the foaming reaction occurs rapidly without the addition of a catalyst. Curing times range from 3 to 6 minutes in the absence of a catalyst. *With* catalyst addition, foams can be demolded in less than two minutes after preparation.

Both cell structure and aesthetic properties of foams produced from HYPOL prepolymer can be controlled by changing the amount of water, type of surfactant, etc. For example:

1. Foams ranging from cosmetic softness to rigid and from conventional open cell structure to fully reticulated.
2. Rapidly wetting to slow, controlled wetting foams can be formed. Such foams absorb and retain from 10 to 30 times their weight of water.
3. Foams with densities of from 2 lbs./ft.³ to 20 lbs./ft.³ can be readily prepared from HYPOL prepolymer. Tensile properties are generally comparable to those of conventional polyurethane.

Such "fine tuning" of their properties with water, surfactants and other additives leads to a great number of possible applications for HYPOL foams. Suggested end uses include: absorbent products; cleaning pads; filters; carpet underlayment; floor and wall coverings; nonwoven binders; disposable absorbent material in babies' diapers and sanitary napkins; medical, dental and cosmetic pads. Other promising applications for the polymer foams are in sound deadening, plant growth media, artificial sponges, and various household items.

The fire retardant properties of HYPOL foams are vastly superior to those of conventional polyurethane foams. The Limiting Oxygen Index (LOI) for HYPOL foams is in the range of 25 to 35 *without additives*, compared with 15 to 18 for conventional foams. This highly desirable HYPOL foam characteristic can be further enhanced by the addition of a flame retardant to the polymer and water mixture.

Further information on technical and application consulting services as well as HYPOL samples and prices may be obtained from A.B. Holmstrom, Commercial Development Manager, Organic Chemicals, Dewey and Almy Chemical Division, W.R. Grace & Co., Whittemore Ave., Cambridge, MA 02140. Tel. 617-876-1400

We know the information given here will be helpful. It is based on our best knowledge, and we believe it to be accurate. Please read all statements, recommendations or suggestions herein in conjunction with our conditions of sale which apply to all goods supplied by us. We assume no responsibility for the use of these statements, recommendations or suggestions nor do we intend them as a recommendation for any use which would infringe any patent or copyright.

GRACE

ATPOL: HYDROPHILIC POLYMER

Foamable Hydrophilic Polyisocyanate

FHP 2000

Amber liquid
(100% active material)

450 – 520

1.19

10,000 – 15,000

1.95 – 2.20

Acetone
Toluene
Trichloroethylene
Ethanol (reacts)
Water (reacts
to form insoluble foam)

Reacts with moisture from the
atmosphere; keep container
tightly capped when not in use.
Crystallizes slowly on long
standing; melts on heating
above 50° C.

Contains minor amount of free
toluene diisocyanate (TDI).
Consult Chemical Safety Data Sheet SD-73,
Manufacturing Chemists Association,
1825 Conn. Ave. N.W.,
Washington, D.C. 20009.
Also see Federal Register,
Vol. 39, No. 125, Thursday,
June 27, 1974, page 23540.

PHYSICAL PROPERTIES

— Appearance —

Equivalent Weight
per NCO Group

Density, 25°C.
g/ml.

Viscosity
cps @ 25°C

NCO Content
meq/g

— Soluble In —

— Storage —
Precautions

— Handling —
Hazards

FHP 3000

Amber liquid
(100% active material)

400 – 450

1.15

15,000 – 20,000

2.2 – 2.5

Acetone
Toluene
Trichloroethylene
Ethanol (reacts)
Water (reacts
to form insoluble foam)

Reacts with moisture from the
atmosphere; keep container
tightly capped when not in use.
Crystallizes slowly on long
standing; melts on heating
above 50° C.

Contains minor amount of free
toluene diisocyanate (TDI).
Consult Chemical Safety Data Sheet SD-
Manufacturing Chemists Association,
1825 Conn. Ave. N.W.,
Washington, D.C. 20009.
Also see Federal Register,
Vol. 39, No. 125, Thursday,
June 27, 1974, page 23540.

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We hope the information given here will be helpful. It is based on our best knowledge, and we believe it to be true and accurate. Please read all statements, recommendations or suggestions herein in conjunction with our conditions of sale which apply to all goods supplied by us. We assume no responsibility for the use of these statements, recommendations or suggestions, nor do we intend them as a recommendation for any use which could infringe any patent or copyright.

Organic Chemicals, Dewey and Almy Chemical Division, W. R. Grace & Co.
Whittemore Avenue, Cambridge, Massachusetts 02140

ORGANIC CHEMICALS

**Dewey and Almy Chemical Division
W. R. Grace & Co.**

**Cambridge, Massachusetts 02140
(617) 876-1400**

FORMULATION

OF

HYPOL[®] FHP 3000 FOAMS

OPERATING PROCEDURES

A. Safety Precautions

Although on a laboratory scale the hazards are small, you should, nevertheless, caution all workers to the vapor hazards of free TDI. With HYPOL FHP prepolymer, only about 1-2% by weight of free TDI is present.

When working in a production line, the TDI vapor hazard is much greater because of larger amounts of materials and longer exposure times for your workers. Be sure that adequate ventilation is provided. The maximum allowable concentration of TDI in the air is 0.02 parts per million, and new government regulations may soon change this to 0.005 ppm.

B. Handling Practices

Please remind workers to protect the FHP prepolymer from unnecessary exposure to moisture from the air. Further, FHP 3000 tends to crystallize slowly on storage and become more viscous. This thickening is reversible and can be eliminated by warming the sample and cooling to room temperature again prior to foaming. To improve the ease of transfer, you should warm the polymer to about 50°C prior to pouring.

C. Foam Formulations

The following recipes correspond to the enclosed small 1" cube foam exhibit samples. Ingredients are listed into two parts, Component A and Component B. After mixing each separately, add part B to part A. Then stir the mixture vigorously for about 20-30 seconds and pour into a mold for foaming. Approximate figures are given for cream time (time for gas bubbles to become visible); rise time; cure time (time for surface to become non-tacky), and demold time.

1. Regular Foam (HYPOL[®] FHP 3000)

The only difference in these preparations is the amount of water used in the foaming operation.

<u>Component A</u>	<u>Component B</u>
100 parts prepolymer FHP 3000	a) 100 parts water, or
1 part L-520 silicone surfactant	b) 80 parts water, or
	c) 50 parts water

Sample 1-a - (100 parts water) had a cream time of 35 seconds, rise time of 220 seconds, cure time of 310 seconds, demold time of 6 minutes. Foam density 4.5 lbs/ft³ after drying.

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(80 parts water) had a cream time of 35 seconds, rise time of 180 seconds, cure time of 330 seconds,³ demold time of 6 minutes. Foam density ~4.1 lbs/ft³

Sample 1-c - (50 parts water) had a cream time of 30 seconds, rise time of 170 seconds, cure time of 320 seconds,³ demold time of 6 minutes. Foam density ~3.9 lbs/ft³

Similar foams can be prepared using no surfactant at all. Cells tend to be rather coarse under these conditions. Foams made without surfactant are more easily wetttable by water and, of course, would be free of traces of extractable surfactant. The foaming speed can be greatly increased by adding Thancat DD (amine catalyst) to the water prior to mixing with the prepolymer. Somewhere around 0.5 to 1.5 parts catalyst per 100 parts water should work out quite well. With this assist you should be able to demold in about 2 minutes.

2. Regular Foam (HYPOL[®] FHP 3000) with Added TDI for Lower Density

The same prepolymer is used as for 1.

Component 2-a
100 parts prepolymer
5 parts TDI
1 part L-520

Component B
100 parts water

Component 2-b
100 parts prepolymer
10 parts TDI
1 part L-520

Component B
100 parts water

Component 2-c
100 parts prepolymer
15 parts TDI
1 part L-520

Component B
100 parts water

Component 2-d
100 parts prepolymer
20 parts TDI
1 part L-520

Component B
100 parts water

Sample 2-a - The cream time was 30 seconds, rise time 250 seconds, cure time 290 seconds and demold time 5 minutes. Foam density ~3.5 lb/ft³.

Sample 2-b - The cream time was 35 seconds, rise time 220 seconds, cure time 420 seconds and demold time 7 minutes. Foam density ~2.5 lbs/ft³.

Sample 2-c - The cream, rise and cure times were comparable to 2-a and 2-b except slightly extended; the demold time was slightly more than in 2-a and 2-b and the foam density was ~2.7 lbs/ft³.

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The cream, rise and cure times were comparable to 2-a and 2-b except slightly extended; the demold time was slightly more than in 2-a and 2-b and the foam density was $\sim 2.3 \text{ lbs/ft}^3$.

An alternate method of lowering foam density is to use an auxiliary blowing agent. We have found that FREON[®] 11 placed into the prepolymer phase serves nicely in most formulations. Densities approaching about 2.0 lbs/ft^3 can be achieved by use of FREON at levels of 5-15 parts/100 parts of HYPOL[®] polymer. FREON blown foams have an additional softness that is difficult to achieve in any other way.

3. Regular Foam (FHP 3000) with Added PAPI 135 (Flexible to Rigid)

The prepolymer is again FHP 3000.

Component 3-a
100 parts prepolymer
100 parts PAPI
2 parts L-520

Component B
100 parts water

Component 3-b
100 parts prepolymer
50 parts PAPI
2.0 parts L-520

Component B
100 parts water

Component 3-c
100 parts prepolymer
8 parts PAPI
2 parts L-520

Component B
100 parts water

Sample 3-a - The cream time was 70 seconds, the rise time was 380 seconds, the cure time was 500 seconds and the demold time was about 11 minutes. Rigid foam, density $\sim 4.1 \text{ lbs/ft}^3$.

Sample 3-b - The cream time was 60 seconds, the rise time was 320 seconds, the cure time was 480 seconds and the demold time about 11 minutes. Semi-flexible foam; density $\sim 3.9 \text{ lbs/ft}^3$.

Sample 3-c - The cream, rise, cure and demold times were slightly less than those recorded in samples 3-a and 3-b. Flexible foam; density $\sim 3.3 \text{ lbs/ft}^3$.

4. Regular ANGEL FOAMTM (FHP 2000) for Softness and Water Wickability

The prepolymer this time is FHP 2000.

Component A
200 parts prepolymer

Component B
90 parts water
10 parts Pluronic L-64

The cream time was 30 seconds, the rise time was 160 seconds, the cure time was 330 seconds and the demold time about 7 minutes. Foam density $\sim 3.5 \text{ lbs/ft}^3$. This foam is rather difficult

make by hand stirring. To get best results, mixing should be done very thoroughly, preferably using a high speed mechanical agitator.

5. Regular Reticulated Foam (FHP 3000)

The prepolymer batch is FHP 3000.

Component A

200 parts prepolymer
15 parts TDI

Component B

190 parts water
10 parts Pluronic L-64
0.5 part Calcotone green pigment

The cream time was 40 seconds, the rise time was 160 seconds, the cure time was 260 seconds and the demold time about 5 minutes. Foam density $\sim 4.1 \text{ lbs/ft}^3$.

D. Compounding Ingredients

For the foam recipes and attachments listed, here are the sources of the compounding ingredients cited therein.

L-520 Silicone Surfactant	- Union Carbide Corporation
PAPI 135 Polyisocyanate	- Upjohn Co.
Monastral Blue Pigment	- American Cyanamid Co.
Calcotone Green Pigment	- American Cyanamid Co.
Pluronic L-64 Surfactant	- BASF Wyandotte Corp.
Thancat DD catalyst (N-ethyl morpholine)	- Jefferson Chemical Co.
FREON [®] 11	- duPont Co.

E. Foaming Equipment

Polyurethane foams are made in the U.S. alone in quantities in excess of 1 billion lbs/year. There has been a lot of work done to devise equipment for foaming. However, with all conventional urethanes only about 2-4 parts/100 of water is used. By way of contrast, in HYPOL[®] foams we use routinely anywhere from 30 to 150 parts/100 of water. So some modifications in equipment are required, although these are relatively minor.

At our labs in Columbia, we have a standard Martin Sweets Co. foam machine in operation with HYPOL[®] prepolymer. This forms loaves or buns by the "pour" method (i.e., no spraying possible with this machine). We also have a Gusmer spray gun. Still another method of foaming is outlined in the attached reprint from Product Engineering, September, 1972. If more information is needed, we would be glad to discuss foaming equipment in more detail.

F. Foam-in-Place Applications

There is the possibility of the coating or impregnating of fabrics (woven and non-woven) with FHP prepolymer, followed by immersion in water (or steam) for foaming in situ.

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... successfully with conventional urethane foams. The unusual compatibility of our FHP prepolymer with water, we believe, that it should be possible, for the first time, to successfully foam in place in this manner. We have had limited success in the laboratory using cotton fabric. However, we recognize that the task is not a simple one and that it will require substantial development effort and skill to develop a satisfactory product and process.

As we are primarily interested in selling the FHP prepolymers, rather than a foamed product, we have not devoted much time to the study of foam-in-place techniques. The only guidance we can give is that the cotton swatches were saturated with FHP prepolymer and the excess polymer squeezed out with a doctor blade (or by nip rollers). The sample was then immersed in warm water (50-60°C) for about 40-50 seconds and removed from the water for completion of the foaming.

After the foam surface has become tack-free, one might consider "crushing" the foam by passing it immediately between nip rollers under moderate pressure. This will help to give a smoother surface, a more uniform thickness control and a coated fabric that will later show dimensional changes (swelling and shrinking) when it is contacted with water or solvents.

This latter foam crushing operation may be useful in gaining the microporous cell structure needed or desired for applications such as fabric coatings, chamois-like products, filters and synthetic leather like products.

G. Skin Embossing

FHP foams can be surface embossed by contacting with a metal pattern surface, preheated to about 200°C or so for 5-15 seconds under light pressure. This heat/contact technique will give an integral surface skin having the same embossed pattern as the metal pattern sheet or mold. Presumably this embossing could be done continuously by passing the foam sheet through heated, patterned nip rollers.

H. Foam/Fabric Laminates

Conventional poly(ester/urethane) foams can be readily slit into thin sheets. These sheets can then be flame laminated (melt bonded) to fabrics or other substrates. This technique has not been done successfully to date with conventional poly(ether/urethane) foams.

Although we have not tried it, we believe that the HYPOL[®] FHP foams may be successfully bonded using the flame lamination method.

Of urethane foams, of course, can be laminated to
or other substrates by the use of adhesives.

Conclusions

I hope that these instructions and samples will give a good
starting point for evaluation of the HYPOLS in your applications.
It takes some practice and experience to be able to make the foams
successfully each time. If you have any problems or questions,
please don't hesitate to get in touch with us.

APPENDIX C

**Grim, K.E. and Linch, A.L. "Recent Isocyanate-
in-Air Analysis Studies." Amer. Ind. Hyg. Assoc.
J. 25: 285-290, 1964.**

**(Reproduced with permission of the American
Industrial Hygiene Association.)**

Recent Isocyanate-in-Air Analysis Studies

K. E. GRIM and A. L. LINCH

Elastomer Chemicals Department, Experimental Station, and the Organic Chemicals Department, Chambers Works, E. I. du Pont de Nemours and Company, Wilmington, Delaware

§ The reagent and sample volumes for the Marcali method for the determination of toluenediisocyanate (TDI) in air have been modified to accommodate the 1961 revision of the Threshold Limit Value (TLV = 0.02 ppm). A lightweight, easily portable assembly which includes the "Uni-Jet" Constant Rate Air Sampler, reagents, and a compact set of permanent liquid color standards for the range 0.01 to 0.06 ppm was developed for field surveys. A similar unit, modified to provide permanent liquid color standards in a visual comparator adapted to the required 10-cm light path, was completed for the Ranta determination of combined TDI and TDI urea. A satisfactory laboratory test, based on the Marcali method for TDI, has been developed for traces of MDI (methylene-bis-(4-phenylisocyanate)) in air. The method easily detects 0.01 ppm MDI in a one cubic foot air sample.

Introduction

THE CONTINUED growth of the urethane foam industry has emphasized the importance of field testing the atmosphere in the vicinity of foaming operations to insure that isocyanate contamination of the air is held to safe limits. The original Marcali field kit¹ is adequate for estimating TDI (toluenediisocyanate) down to 0.05 ppm. However, the revision of the Threshold Limit Value for TDI in air from 0.1 to 0.02 ppm in 1961 by the American Conference of Governmental Industrial Hygienists² placed the TLV below the applicable limit of the field kit.

An alternate test method, the Ranta Method,³ permits the simultaneous determination of TDI and TDI urea (3,3'-diisocyanate-4,4'-dimethylcarbanilide). Although this method was used in the laboratory to follow the original toxicological studies of TDI,² no test kit had been developed for field use.

Isocyanates other than TDI are finding increased use in urethane foam formulations. Notable among these newer isocyanates is MDI (methylene-bis(4-phenylisocyanate)), for which neither the Marcali nor the Ranta method is directly applicable.

This paper presents: (a) modifications of the Marcali field kit to permit the determination of TDI in air down to 0.01 ppm; (b)

a field kit based on the Ranta method for determining TDI plus TDI urea in air down to 0.01 ppm; (c) a laboratory method, which should be easily adaptable to a field test kit, for rapidly determining MDI in air down to 0.01 ppm.

TDI Field Kits

The field kit devised by Marcali was not intended to determine TDI in the 0.02 ppm range, but a review of the method indicated that by increasing the air sample size and decreasing the reagent volumes adequate sensitivity could be obtained. A similar adjustment of air volume and the use of long-path colorimetric standards permit the use of the Ranta method in a portable field kit. Both methods described below were developed in cooperation with the Union Industrial Equipment Co., Port Chester, New York.

Improved Sampler

The use of a hand operated sampling device for large air samples has several disadvantages. Collection of a one-cubic-foot sample under the conditions originally recommended would require 30 minutes of tedious work and full time attention by an operator to a single sampler. These objectionable features have been overcome by

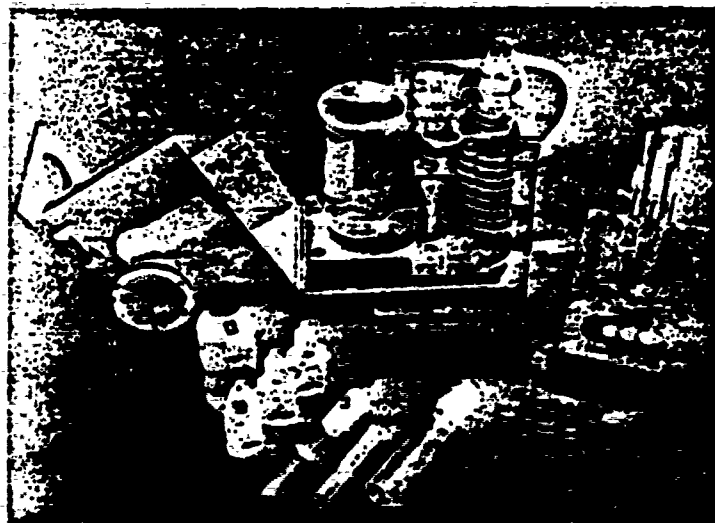


FIGURE 1. "Uni-Jet" Air Sampler and TDI test kits.

using the self-powered "Uni-Jet"¹ Constant Rate Air Sampler.¹ This collector (Figure 1) derives the vacuum required to draw the air sample through a standard midjet impinger by expansion of "Freon-12"² or "Freon-22" propellants (for low ambient temperatures) through a microaspirator. Constant aspirating rate is provided by a back-pressure controlled liquid "Freon" feed valve which maintains a constant propellant vapor pressure at the aspirator nozzle orifice. It provides a uniform sampling rate over an ambient temperature range of 30°-110°F with the absence of spark or static sources. The only operational attention required is the opening and closing of the propellant control valve.

The standard midjet impinger was modified by installing a "Teflon"³ fluorocarbon resin baffle to minimize entrainment and by placing a "Teflon" sleeve over the standard taper joint to eliminate the need for lubricant.

Sensitive TDI Test Kit

The preferred method for the determination of TDI in air is the Marcali method.^{1,2} This colorimetric method depends upon the hydrolysis of the isocyanate to the corresponding amine, diazotization and coupling to *N*-1-naphthylethylenediamine and measurement of the color intensity at 550 millimicrons.

The reagents and chemical manipulations of the original Marcali method were retained. Improvement in sensitivity by increasing the air volume sampled and reducing the reagent volume is summarized in Table I; the equipment is illustrated in Figure 1.

Since the reagent solutions are stable for no more than two or three weeks, the solid components are enclosed in sealed glass capsules placed within the plastic container along with the appropriate volume of water or aqueous acid. Just prior to use, the capsules are crushed by finger pressure against the sides of the bottles and the solid component dissolved by shaking before removing the bottle caps. The reagents are dispensed dropwise from plastic bottles through capillary tips which deliver reproducibly uniform drop sizes (0.01 ml/drop).

Permanent, stable, liquid color standards (0.01, 0.02, 0.04, and 0.08 ppm) which match the dimensions and contour of the tube in which color development is carried out are sealed in a pocket-size (1¼ x 3¼ x ¾ inches) color comparator block. Sufficient reagents for eight to ten field tests and the color comparator can be obtained commercially as a complete kit.⁴

Since the hydrolysis of TDI to toluenediamine in the acid absorber solution is essentially quantitative, calibrations may be

checked by use of an equivalent amount of toluenediamine (MTD) in place of the relatively hazardous isocyanate derivative which requires special precautions for quantitative transfers. Multiply the micrograms of MTD by 1.43 to obtain the equivalent micrograms of TDI.

Precision, accuracy and sensitivity are well within limits imposed by visual color density comparison ($\pm 10\%$ probable range). Greater accuracy and sensitivity can be attained by spectrophotometric determination but the ambient physical variables encountered in most industrial air surveys do not justify the additional time, effort and equipment required.

Procedure

Measure 8.0 ± 0.2 ml of acid absorber solution into the calibrated test tube and pour it into the midjet impinger. Then connect the midjet impinger to the "Uni-Jet" Air Sampler, place it in the coil cavity and aspirate the air at 0.1 cu. ft. per minute for 10 minutes.

Disassemble the midjet impinger and measure 4 ml of the absorber solution into the calibrated test tube. Crush the glass vials in the small plastic bottles containing solutions 1, 2, and 3 and shake vigorously to effect solution. Open the bottles to uncover the dropping tips, and add three drops of solution No. 1 (sodium nitrite-bromide reagent). Mix by closing the tube with the rubber stopper and inverting several times.

After two minutes, add six drops of solution No. 2 (sulfamic acid) and swirl until most of the gas is evolved. Stopper and invert several times. Release the stopper carefully to prevent spattering.

Add six drops of reagent No. 3 (N-1-naphthylethylenediamine), stopper and invert several times. A blue-red color indicates TDI is present. (A transient color which disappears indicates incomplete removal of the nitrite; repeat the test with the remaining 1 ml of absorber solution.)

Dilute to 5 ml with the absorber solution and mix. After three minutes, compare the color with the sealed liquid color standards in the comparator. The standard which most

TABLE I
Field Kit for the Marcoll Determination
of TDI in Air Showing Revisions

Dimension	Marcoll	Revision
<i>Marcoll Method</i>		
Volume of air sample, cu. ft.	0.1	1.0
Sampling rate, cfm	0.033	0.10
Sampling time, min.	3	10
Absorber solution	15	5
Volume, ml		
Volume 0 ml for color	15	4
Development, ml		
Reagent volume		
Sodium nitrite	0.5 ml	3 drops
Sulfamic acid	1.0 ml	6 drops
N-Naphthylethylenediamine	1.0 ml	6 drops
Final volume, ml	20	5
Color standards, ppm	0.05-0.2	0.01-0.05

nearly matches the sample represents the amount of TDI in parts per million.

If the color density is greater than the 0.08 ppm standard, mix the solution with the material remaining in the impinger and compare the resulting solution to the standards. Multiply the standard values by two.

Ranta Method

The Ranta method, which measures TDI and TDI urea, depends upon the spectrophotometric measurement of the yellow color (450 m μ) formed when dimethylcarbanilide is absorbed in an aqueous solution of ethyl cellosolve, sodium nitrite and boric acid. The low intensity of the yellow color previously made its adaptation to a field kit impractical. However, sufficient sensitivity was obtained by increasing the volume of air sampled to one cubic foot, reducing the absorber volume to 10 ml, and increasing the light path in the colorimeter to 100 mm. The visual comparator incorporating the long light path is shown in Figure 1. Light enters the tubes at the top and is viewed as discrete circles in the mirror mounted in the base of the comparator block. Both the reagent kit and color standards are now commercially available.⁴

Procedure

Crush the glass capsule inside the plastic reagent bottle and shake to effect solution of the sodium nitrite. Remove the plastic seal and measure 10 ml of acid absorber solution into the midjet impinger. Connect the impinger to the "Uni-Jet" Air Sampler, place it in the cavity coil and aspirate air at 0.1

cu. ft. per minute for 10 minutes. Disassemble the impinger and allow it to stand for 20 to 30 minutes at room temperature.

Place the sample in the visual comparator and match with the appropriate standard color. The comparator is used most effectively by tilting it until three circles of light appear in the diagonally installed mirror.

Spectrophotometric Determination of MDI

The advent of MDI into the foam-formulation market has increased the need for a convenient, sensitive method for analysis of that material in air. A survey of the applicability of the Marcali method conducted in this laboratory revealed the absorption and diazotization were satisfactory but the coupling reaction proceeded so slowly the procedure was inconvenient.

Investigation of the concentration of the coupler solution and acidity during the coupling reaction led to modifications which reduced the final reaction time from two hours to fifteen minutes. The chemistry appears to be the same as that of the Marcali TDI test: the MDI is hydrolyzed to MDA (methylene dianiline), diazotized and coupled to *N*-1-naphthylethylenediamine.

Apparatus

Spectrophotometer: Cary Model 14, Beckman Model B, or any equivalent spectrophotometer.

Cells: 5-cm matched quartz cells.

Sampler: "Uni-Jet" Air Sampler with standard midjet impinger as previously described.

Reagents

Sodium nitrite-Sodium bromide solution. Dissolve 3.0 gm sodium nitrite and 5.0 gm sodium bromide in water and dilute to 100 ml.

Sulfamic Acid. Dissolve 10.0 gm sulfamic acid in 90 ml water.

Absorber Solution. Add 35 ml concentrated hydrochloric and 22 ml glacial acetic to about 600 ml water and dilute to one liter with water.

Coupling Solution. Dissolve 1.0 gm *N*-1-

naphthylethylenediamine dihydrochloride in 50 ml water, add 2 ml concentrated hydrochloric acid and dilute to 100 ml with water. This solution is stable for about ten days.

Sodium Carbonate. Dissolve 16.0 gm sodium carbonate in water and dilute to 100 ml.

Procedure

Collection of Sample. Pipet 15 ml of the acid absorber solution into a midjet impinger. Connect the impinger to the "Uni-Jet" Air Sampler and place it in the coil cavity. Aspirate the air sample through the absorber solution at 3 liters per minute. Note the length of time and calculate the actual sample size. The estimated ideal sampling time may be computed as follows:

$$\text{Minutes to sample} = 0.25 / \text{expected ppm MDI}$$

Color Formation. Pipet 0.5 ml sodium nitrite solution into the impinger, stir well and allow to stand for two minutes. Then pipet 1.0 ml 10% sulfamic acid solution into the impinger and stir for 30 seconds. After about two minutes, pipet 1.5 ml sodium carbonate solution into the impinger and stir. Add 1.0 ml coupler solution with stirring. After 15 to 30 minutes, measure the absorbance against a blank at 555 m μ . Refer to the calibration curve to find the micrograms of MDI in the sample.

Calibration Curve.

Solution A. Accurately weigh 0.25 to 0.30 g MDI into 700 ml of glacial acetic acid. Agitate to dissolve and dilute to one liter with water.

Solution B. Immediately pipet 10 ml Solution A into a one-liter volumetric flask, add 35 ml concentrated hydrochloric acid, 15 ml glacial acetic acid, and dilute to the mark with distilled water. This solution contains 2.5 to 3 μ g MDI/ml.

Pipet 0.5, 1.0, 2.0, and 5.0 ml of Solution B into midjet impingers containing 14.5, 14.0, 13.0, and 10.0 ml of absorber solution respectively. Proceed with the color formation as described previously. Plot absorbance

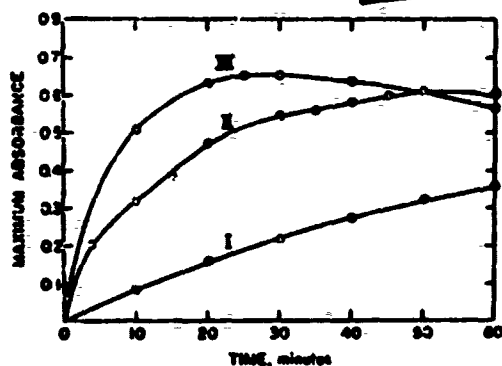


FIGURE 2. Effect of *N*-1-Naphthylethylenediamine concentration on color reaction time (10.6 micrograms of MDI). Curve I at 0.1%; II at 0.4%; and III at 1.0%.

at 555 m μ against micrograms of MDI to obtain the calibration curve.

Calculations.

$$\text{ppm MDI} = 97.8 (W/V)$$

where:

V = total sample volume in milliliters, and
 W = weight of MDI in micrograms.

Experimental

Effect of Coupling Solution Concentration.

The concentration of the *N*-1-naphthylethylenediamine coupling solution concentration recommended for TDI was 0.1%. A study showed the time for complete color formation could be reduced from two hours to 30 minutes by increasing the concentration to 1.0% (Figure 2). Further increase in concentration is impractical due to the solubility of the *N*-1-naphthylethylenediamine.

Effect of Acidity on Color Formation.

Since normal coupling reactions proceed more rapidly in a less acid solution and the diazo compound is less stable in an alkaline solution, the acidity of the coupling media was investigated.^{2,3,4} A 0.4M acetic acid scrubber solution was substituted for the solution 0.4M in both acetic and hydrochloric acids; the maximum color formation was attained more quickly but faded (Figure 3). Partial neutralization of the hydrochloric-acetic scrubber solutions yielded a stable color and further reduced the coupling time from

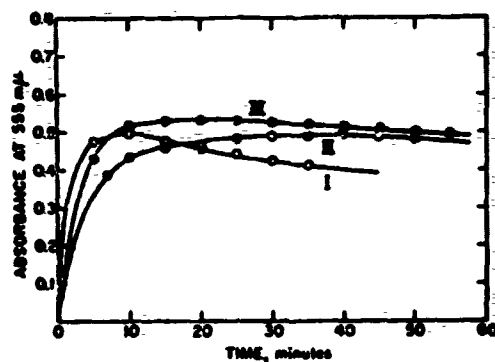


FIGURE 3. Effect of acidity on time of formation and decay of color during the coupling reaction using a 1% coupler solution. Curve I: HCl omitted from original absorption solution. Curve II: Normal absorption solution (0.4M in both HCl and acetic acids); 0.5 ml of 1.5M Na_2CO_3 added before coupling reagent. Curve III: Absorption solution as above with 1.5 ml of Na_2CO_3 solution added.

30 to 15 minutes. Careful investigation demonstrated that a 20% error in the sodium carbonate solution will make only a small difference in the intensity of the color but further deviation can seriously affect the results. For example, when 2.0 ml of sodium carbonate is used, no color develops.

Spectral characteristics of color. The maximum absorbance was at 565 m μ for the MDI analysis by the unmodified Marcell method rather than at 550 m μ as reported for TDI. However, in the more alkaline solution, the maximum shifts down to 555 m μ .

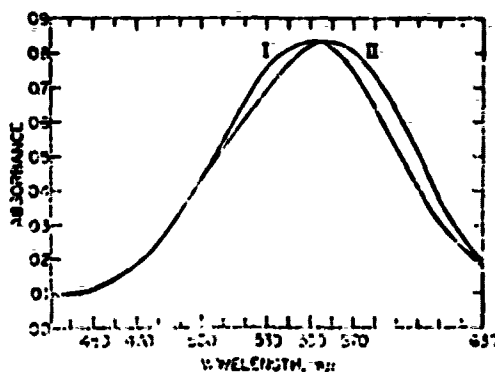


FIGURE 4. Visible absorption spectra obtained for analysis of TDI (Curve I) and MDI (Curve II).

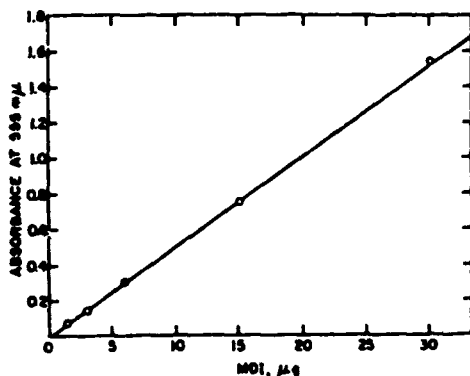


FIGURE 5. Calibration curve for methylene-bis-(4-phenylisocyanate).

for MDI and gives a spectrum very similar to that of TDI (Figure 4). The absorptivities for the TDI and MDI determination are very similar ($a_{590 \text{ m}\mu}$ for TDI = 186 liters/gm-cm; $a_{518 \text{ m}\mu}$ for MDI = 189 liters/gm-cm). Beer's Law is obeyed to at least 30 micrograms of MDI (Figure 5).

Discussion

Analyses of standard solutions containing 1.5 to 8 micrograms of MDI (equivalent to 0.005 to 0.03 ppm MDI in a one-cubic-foot sample of air) were performed on two instruments using their respective calibration curves and showed the 95% confidence limits for the average of duplicates to be ± 0.14 micrograms of MDI for the colorimetric method. An absorbance of 0.01 on a ten-liter

sample represents 0.002 ppm MDI. The similarity of colors obtained in the determination of MDI and TDI prompted preliminary experiments which indicate the procedure just described can be modified to give an estimate of the MDI in air using the existing "Unico" TDI test kit colors. The additional reagents required are a 1.5M sodium carbonate solution and a 1% N-1-naphthylethylenediamine dihydrochloride solution.

Acknowledgements

Thanks are gratefully extended to S. S. Lord, Jr. and L. W. Hicken for the invaluable assistance rendered during this investigation.

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APPENDIX D

**RECOMMENDATIONS FOR A TOLUENE
DIISOCYANATE STANDARD**

I. RECOMMENDATIONS FOR A TOLUENE DIISOCYANATE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to toluene diisocyanate (also called tolylene diisocyanate or TDI) in the workplace be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for an 8-hour day, 40-hour week over a working lifetime. Compliance with the standard should therefore prevent adverse effects of TDI on the health and safety of workers except in those workers already sensitized to TDI; they should not be exposed to any amount at all. The standard is measurable by techniques that are valid, reproducible, and available to industry and governmental agencies. Sufficient technology exists to permit compliance with the standard. The standard will be subject to review and will be revised as necessary.

"Exposure to toluene diisocyanate" includes work in any area where toluene diisocyanate is stored, transported, or used.

Section 1 - Environmental (Workplace air)

(a) Concentration

Occupational exposure to toluene diisocyanate (TDI) shall be controlled so that no worker shall be exposed to a time-weighted average (TWA) of more than 0.005 ppm (0.036 mg/cu m) for any 8-hour workday or for any 20-minute period to more than 0.02 ppm (0.14 mg/cu m).

(b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis of TDI samples shall be as provided in Appendices I and II, or by methods shown to be equivalent or better in sensitivity, precision, and accuracy.

Section 2 - Medical

(a) Medical Examinations

(1) Preplacement: A comprehensive physical examination for all workers shall be made available to include as a minimum: medical history, a 14" by 17" chest roentgenogram, total white blood cell count with differential, baseline forced vital capacity (FVC) and forced expiratory volume at one second (FEV 1.0). An absolute eosinophil count on capillary blood is recommended as an additional useful baseline measurement. The history should pay particular attention to the presence and degree of any respiratory symptoms, ie breathlessness, cough, sputum production, wheezing, and tightness in the chest. Smoking history should also be elicited.

If a positive personal history of respiratory allergy, previous sensitization to TDI, or chronic obstructive pulmonary disease is elicited, the applicant shall be counseled on his increased risk from occupational exposure to TDI. Chronic bronchitis, emphysema, disabling pneumoconiosis, or cardiopulmonary disease with significantly impaired ventilatory capacity similarly suggest an increased risk from exposure to TDI. If a history of allergy other than respiratory or of other chronic respiratory disease is elicited,

the applicant should be counseled by the physician that he may be at increased risk of adverse health effects from industrial exposure to isocyanates. At the time of this examination, the advisability of the worker's using negative or positive pressure respirators shall be evaluated.

(2) Periodic: The above examinations (with interim history), with the exception of the chest roentgenogram, shall be provided annually, or as otherwise indicated by professional medical judgment, so long as occupational exposure to TDI continues. Repeat white cell counts with differential and absolute eosinophil counts on peripheral blood may also be useful. An estimation of FVC and FEV 1.0 at the beginning and the end of a work shift within the first six months of employment with TDI is recommended as a useful means of surveillance for TDI reaction. Diagnosis of sensitization to isocyanates, for example from the occurrence of acute asthma, nocturnal dyspnea, nocturnal cough, or eosinophilia, at any time including annual periodic evaluations should exclude the worker from further exposure to isocyanates.

Because of seasonal variations in pulmonary function, it is desirable, for comparison of changes in respiratory function, that the periodic examination of an individual worker be performed about the same time each year.

(3) The periodic medical program required in (2) above should be considered a minimal program. In addition, changes in processes or the occurrence of spills or other emergencies that may

cause changes in normal exposure levels, such as brief, high, excursions, should be reported to the responsible physician, who may require additional medical examinations or other medical procedures.

A decrement in FEV 1.0 as measured before commencement of the work-shift and again after completion of the work-shift is a valuable indication of specific reaction to TDI at the operational exposure level. A rise in eosinophil count may also provide evidence of a sensitization phenomenon.

(b) Medical Records

Medical representatives of the Secretaries of Health, Education and Welfare and of Labor, and of the employer, and those physicians designated and authorized by the employee shall have access to medical records, which shall include records of all required examinations. These records shall be kept for 20 years, or, if the employee dies sooner, one year after his death.

Section 3 - Labeling (Posting)

Containers of toluene diisocyanate shall carry a label stating:

TOLUENE DIISOCYANATE

DANGER! HARMFUL IF INHALED

CAUSES BURNS

MAY CAUSE SKIN OR

RESPIRATORY REACTION

Do not breathe vapor.

Do not get in eyes, on skin, on clothing.

Keep container closed.

Use with adequate ventilation.

Wash thoroughly after handling.

First Aid: In case of contact immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician immediately.

If TDI is inhaled, remove the victim to fresh air. If not breathing give artificial respiration; if breathing is difficult, give oxygen. Call a physician immediately.

Work areas where exposure to toluene diisocyanate is likely to occur shall be posted with signs stating:

TOLUENE DIISOCYANATE

(TDI)

DANGER

UNAUTHORIZED PERSONS KEEP OUT

HARMFUL IF INHALED

CAUSES BURNS

MAY CAUSE SKIN

OR RESPIRATORY REACTION

Also, the sign shall give information on the location of respirators.

Section 4 - Personal Protective Equipment and Work Clothing

Subsection (a) shall apply whenever a variance from the standards recommended in Section 1 is granted under the provisions of the Occupational Safety and Health Act or in the interim period during the application for a variance. Until the limits of exposure to TDI

in paragraph (a) of Section 1 are met by limiting the concentration of TDI in the work environment, an employer must utilize, as provided in subsection (a) of this Section, a program of respiratory protection to effect the required protection of every worker exposed.

(a) Respiratory protection

Engineering controls shall be used wherever feasible to maintain TDI vapor or particulate concentrations below the prescribed limits. Appropriate respirators shall be provided and used when a variance has been granted to allow respirators as a means of control of exposure to routine operations and while the application is pending. Administrative controls can also be used to reduce exposure to TDI. Respirators shall be provided and used for nonroutine operations (occasional brief exposures above the limits and for emergencies); however, for these instances a variance is not required but the requirements set forth below continue to apply. In addition, appropriate respirators and protective work clothing shall be provided to and used by employees involved in spray operations, as specified below. Appropriate respirators as described in Table I-1 shall only be used pursuant to the following requirements:

(1) To determine the class of respirator to be used, the employer shall measure the atmospheric concentration of TDI in the workplace when the initial application for variance is made and thereafter whenever process, worksite, climate or control changes occur which are likely to increase the TDI concentration; this requirement shall not apply when only positive pressure respirators

will be used. The employer shall ensure that no worker is being exposed to TDI in excess of the standard either because of improper respirator selection or improper respirator fit.

(2) A respiratory protective program meeting the general requirements outlined in Section 3.5 of the American National Standard for Respiratory Protection, ANSI Z88.2-1969, shall be established and enforced by the employer.

(3) Respiratory protective devices described in Table I-1 shall be either those approved under the following listed regulations or those approved under 30 CFR 11, published March 25, 1972:

Gas mask--30 CFR 13 (Bureau of Mines Schedule 14F)

Type C continuous-flow, supplied air respirator--
30 CFR 12 (Bureau of Mines Schedule 19B)

Self-contained breathing apparatus--30 CFR 11
(Bureau of Mines Schedule 13E)

(4) Workers engaged in spraying material containing TDI and others within 10 feet of the spray unit shall wear Type C continuous-flow, supplied air, positive-pressure, impervious hoods. These shall also be worn in field and construction work where TDI is being used in pour, froth, or insulation operations. Use of such respiratory protective equipment does not eliminate the need for adequate ventilation for vapor control, but is additional protection from mist. Gas masks may be used at distances greater than 10 feet from the spray operations if it is shown that the concentration of TDI

Table I-1

Respirator Selection Guide for Protection Against TDI

Multiple of TWA Limit	Respirator Type
Less than 100 X	Gas mask, industrial size combination canister for organic vapors and with high efficiency filter.
Less than 100 X	Type C demand type (negative pressure) supplied air respirator with full face-piece.
Less than 1000 X	For routine (nonemergency) use: Type C continuous-flow (positive pressure) supplied air respirator with full face-piece
Greater than 1000 X (and at lower concentrations)	For emergency use: Self-contained breathing apparatus, in pressure demand mode (positive pressure).

does not exceed 100 times the time-weighted average for continuous work, or 100 times the ceiling for work of short duration, eg 20 minutes or less.

(5) The employer shall provide respirators in accordance with Table I-1 and shall assure that the employee uses them when required. Employees shall be instructed on the use and cleaning of respirators assigned to them, and how to test for leakage.

(b) Protective Work Clothing

(1) Where there is likelihood of skin contact with liquid TDI the employer shall provide employees with impervious clothing. These garments shall be cleaned inside and out each time they are used. Rubber shoes or rubbers over leather shoes shall be worn where there is possibility of foot contact with liquid TDI. Rubbers shall be decontaminated and ventilated after contamination. Leather shoes which have been contaminated with TDI shall be decontaminated or disposed of.

Workers within 10 feet of spray operations, or at greater distances when there is a greater drift of spray, shall be protected with impervious clothing, gloves, and footwear in addition to a supplied air impervious hood.

(2) Chemical workers' goggles shall be worn where splashes are likely to occur.

Section 5 - Appraisal of Employees of Hazards from Toluene Diisocyanate

Each employee exposed to TDI shall be apprised of the hazards, relevant symptoms, and proper conditions and precautions concerning use or exposure. In addition to the better known symptoms, nocturnal dyspnea or nocturnal cough should be mentioned as less obvious symptoms of TDI reaction. The information shall be kept on file and readily accessible to the worker at all places of employment where TDI is manufactured or used. Information as specified in Appendix III shall be recorded on U. S. Department of Labor Form OSHA-20, "Material Safety Data Sheet", or on a similar form approved by the Occupational Safety and Health Administration, U. S. Department of Labor.

Section 6 - Work Practices and Control Procedures

(a) Containers of toluene diisocyanate shall be examined for leaks upon arrival. The containers shall be properly closed at all times when not in actual use. Workers shall wear chemical safety goggles while handling liquid toluene diisocyanate, and protective clothing where contact is likely.

(b) All spills shall be cleaned up promptly in accordance with the procedures described in Part VI. A supply of materials to facilitate clean-up operations shall be kept on hand in all areas where toluene diisocyanate is regularly used.

(c) Waste materials containing toluene diisocyanate can be removed to an isolated area in the open air or with exhaust ventilation and soaked with 10% ammonia-in-water mixture for 24 hours

before discarding. (Caution: Do not tightly close containers used for decontamination, because of a possible increase in gas pressure.)

(d) All employees working in areas where toluene diisocyanate is regularly used shall be instructed in procedures to be used in the event of spills, and shall be instructed in the types of protective equipment to be used during both normal and emergency conditions.

(e) Individuals not having legitimate reasons to be in the TDI work area shall not be allowed access.

(f) Local exhaust ventilation shall be employed wherever possible in indoor operations where toluene diisocyanate is used. Such ventilation shall be designed to prevent the vapor from reaching the breathing zone of workers and shall be maintained in proper working order.

(g) Procedures including fire-fighting procedures shall be established and implemented to meet foreseeable emergency events. Fire fighters shall be cautioned that toxic products, such as hydrogen cyanide, phosgene, and carbon monoxide can be formed from the pyrolysis of polyurethane products, and be prepared to avoid exposure to such products, as well as to TDI. Respirators shall be available for wearing during evacuation if long distances need to be traversed; supplied air respirators shall be available for use where equipment or operations cannot be abandoned.

Section 7 - Sanitation Practices

(a) Washing Facilities

Emergency showers and eye fountains shall be provided in areas

where there is a potential exposure to toluene diisocyanate. They shall be inspected frequently to make sure that they are in proper working condition.

(b) Food Facilities

Food preparation and eating should be prohibited in toluene diisocyanate areas. Smoking in such areas should also be prohibited.

(c) Clothing

Workers should change into work clothing at the start of work, and remove it at the end of the workday.

Clothing on which toluene diisocyanate has been spilled shall be placed in a tightly sealed container until removal for laundering. The employer shall provide for laundering such clothing. If commercial laundering facilities are used, the employer shall inform the launderer of the precautions required in handling such clothing.

Section 8 - Monitoring and Recordkeeping Requirements

(a) Employers shall monitor environmental exposures to TDI based upon the following sampling schedule:

(1) Monthly requirements: Except as otherwise indicated by a professional industrial hygiene survey, breathing zone samples shall be collected at least monthly to permit construction of a time-weighted average exposure for every operation in which there is a potential for exposure to airborne TDI, so that each employee or employee location is sampled at least once every 6 months.

(2) Weekly requirements: If monthly sampling shows the time-weighted average (0.005 ppm) or ceiling (0.02 ppm) values to

be exceeded at any employee station, immediate steps shall be taken to reduce the exposure. Weekly sampling of that station shall be instituted and continued until all samples for two consecutive weeks meet the standard.

Monitoring shall also be performed weekly whenever there is a change in process or in materials used that could result in increased exposure of workers. Such weekly sampling shall be performed until all samples for two consecutive weeks meet the standard.

(b) Records shall be maintained for all sampling schedules and shall include the type of personal protective devices in use, if any, and the sampling and analytical methods in use. Records shall be classified or readily classifiable by employee, so that each employee has reasonable access to records of his own environmental exposure.

These records (and records of all required medical examinations) shall be maintained for 20 years, or, if the employee dies sooner, one year after his death.